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***Ab initio* Quantum Chemical and Experimental Reaction Kinetics Studies in the Combustion of Bipropellants**

Ghanshyam L. Vaghjiani*

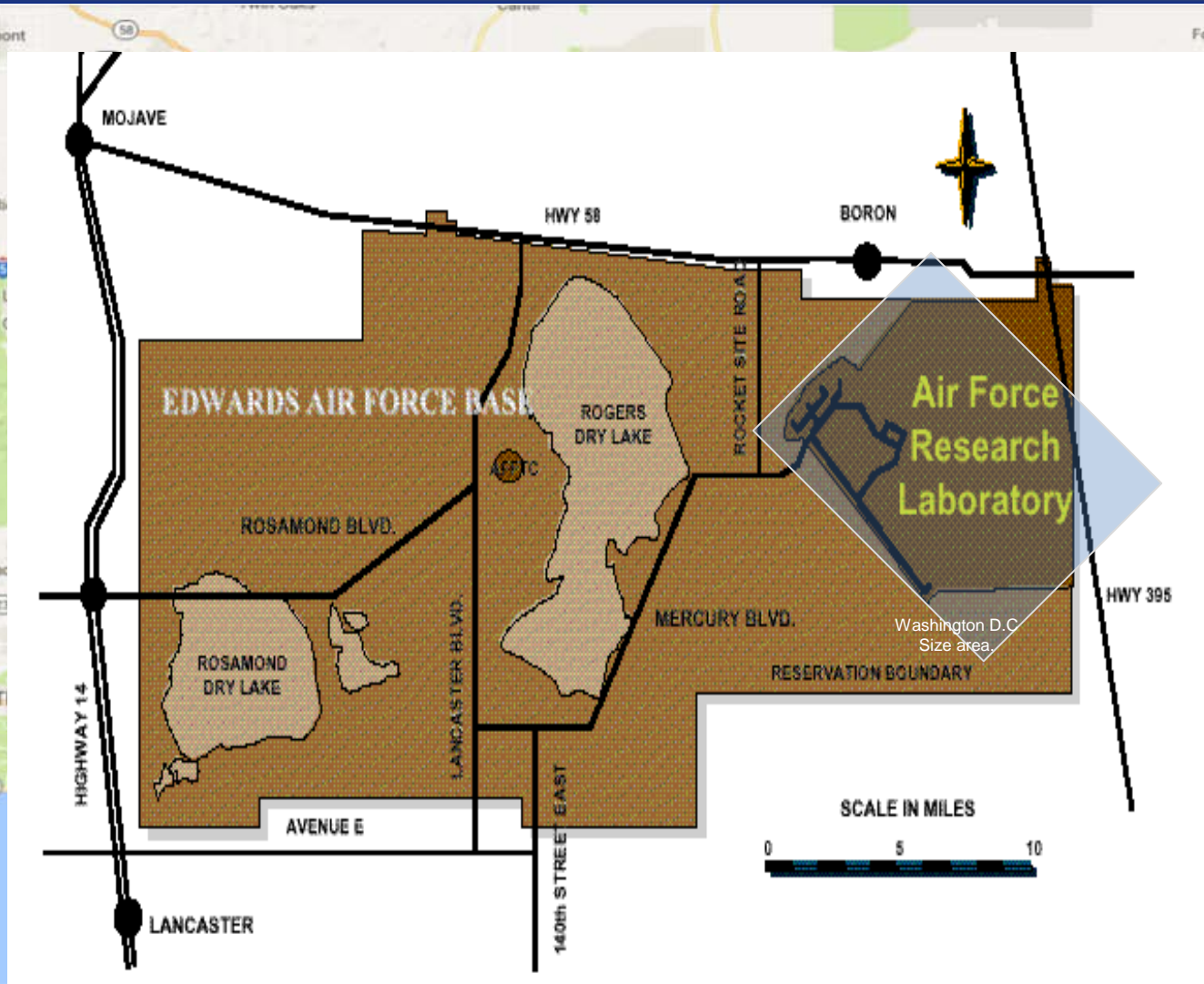
***University of Central Florida
March 24, 2017***

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Where and how big is AFRL at Edwards AFB?





Premier Rocket Test Facilities (+\$3B) In Beautiful Mojave Desert, CA



A Cool Place to Work for a Place That's Hot!

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Edwards AFB Accolades too Many But, e.g., Visit the URLs.....



Murphy's Laws



"If anything can go wrong, it will"
Phrase born in 1949, **EAFB**
Capt. Edward A. Murphy
Engineer working on AF Project MX981
How much sudden deceleration
a person can stand in a crash

<http://www.af.mil/News/ArticleDisplay/tabid/223/Article/137793/rocket-test-stand-gets-facelift.aspx>

<http://www.militarymuseum.org/EdwardsAFB.html>

F-1 Engine Testing **EAFB** Rocket Site



Saturn V



Testing and Early Landings **EAFB**



EAFB Rocket Site Viewing



Apollo, KSC Transporter



EAFB's success is KSC's success!

Chuck Yeager



First human to officially break the sound barrier
October 14, 1947, **EAFB**
Flew the experimental Bell X-1
A **rocket-engine** powered airplane
Mach 1 at an altitude of 45,000 ft

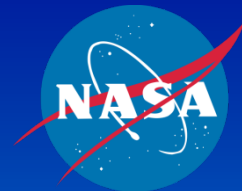


Shuttle Takeoff, KFC





Our Partners in Propulsion Research & Technology Development





Rocket Propulsion for the 21st Century (RP21) Goals



Boost and Orbit Transfer Propulsion

	2017	2027	Status
• Reduce Stage Failure Rate* (RP)	75%	75%	Baseline (B)
• Improve Mass Fraction (Solid)	18%	38%	5%
• Increase ISP % (Solid/Liquid* (RP))	2%/0%	5%/4%	1%/B
• Increase Thrust to Weight % (Liquid, (RP))	103%	103%	10%
• Reduce Engine Turn Time(Reusable)	<8hrs	<4hrs	B
• MTBO/MTBR (Missions, Liquid)	50/100	50/100	10%
• Decrease Motor Health State Uncertainty	20%	50%	10%

Spacecraft Propulsion

• Increase Efficiency (ET/ES/EM)	15%/15%/10%	65%/35%/30%	B/B/B
• Decrease EP System Dry Mass (ET/ES/EM)	0%/50%/50%	75%/90%/90%	B/B/25%
• Decrease Flexible Prop System Wet Mass	35%	65%	B
• Increase Chemical Prop. Density Isp	5%	15%	<1%
• Decrease Chemical Prop. Dry Mass	10%	40%	B

Tactical Propulsion*

• Increase Total Impulse (RS&Smokey/MS)	20%/33%	35%/45%	B
• 4 Pulse motors			
• RS/Smokey Total Impulse Penalty	10/Mf	0	B
• Minimum Smoke Increase Total Impulse	5%	25%	B
• Increase Density Isp	5%	7%	B
• Insensitive Munitions*			

See JIMTP & Backup Information

* Additional Backup goal information exists



In-Space Propulsion (RQRS) R&D

Basic Science to Flight Demo



Sustainment

Resiliency

Superiority

Hall Effect Thruster (HET)

- XR-5A thrusters
- Customer: AFSPC
- Rapid tech transition via agile space experiments



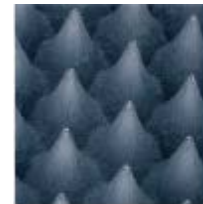
High Power (>100 kW class) EP (FRCs)

- *Extremely low mass, high thrust*
- *multimode compatible*



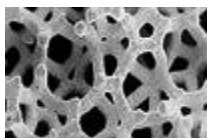
Densified Ionic Liquid Electrosprays (DILE)

- *Cube sat applications*
- *Extremely high efficiency, scalable thrust*



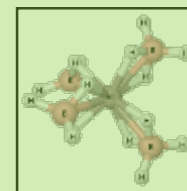
AF-M315E Transition (GPIM)

- Replacement of hydrazine with higher performance non-toxic propellant
- Customer: NASA/AF/Industry
- Developing family of thrust levels ¼ to 20 lbf



Next-gen Adv Biprop Thruster (ABT)

- *More performance*
- *Vol-limited spacecraft*





STEM Students

How to Work at AFRL EAFB?



- **Ph.D**

- **NRC Post-doc**

- <http://nrc58.nas.edu/RAPLab10/Opportunity/Opportunity.aspx?LabCode=13&ROPCD=133003&RONum=B7679>

- **Graduate Students**

- **AF SFFP**

- <http://nrc58.nas.edu/RAPLab10/Opportunity/Opportunity.aspx?LabCode=13&ROPCD=133003&RONum=B7679>

- **AFIT**

- <http://afsffp.sysplus.com/SFFP/contact/afit-wright-patterson-air-force-basement.aspx>

- **SMART**

- <http://www.asee.org/fellowship-programs/graduate>

- **USAFA**

- <http://afsffp.sysplus.com/SFFP/contact/usafa-colorado-springs-co.aspx>

- **Under Graduate Students**

- **Pathways**

- <https://www.usajobs.gov/GetJob>

- **Student-teachers**

- **STAR**

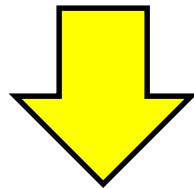
- <http://starteacherresearcher.org/sites.html>



Our Interest in Combustion Kinetics of Bipropellants



- Understand Auto-ignition Chemistry
 - Occurs at Low Temperature-Pressure Conditions
- Understand Fuel Pyrolysis
 - Competes With Oxidation
- Understand Fuel Oxidation
 - Competes With Pyrolysis
- Construct Comprehensive Reaction Kinetics Models
 - Discover Other Auto-igniting Bipropellant Systems



Improve Propulsion Capabilities Over the Current State-of-the-art $\text{CH}_3\text{NHNH}_2/\text{N}_2\text{O}_4$

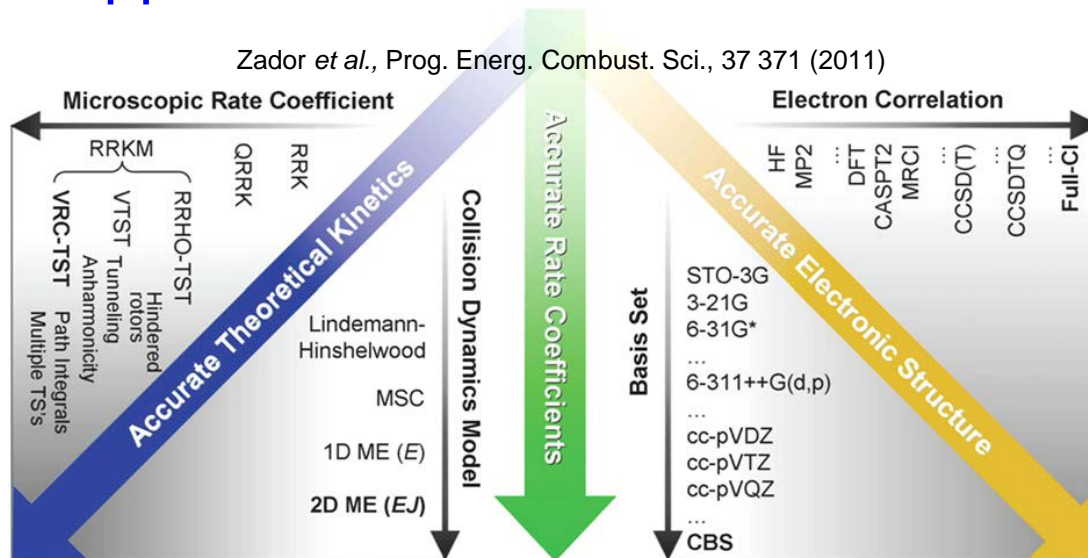




Why Quantum Chemical Reaction Kinetics Studies?



- Only Option When Experiments are not Possible or Limited
 - Combustion Conditions of P & T too Extreme to Probe
- Accuracy (E_a) can be as Good or Better Than Experiments
 - Thermochemical Accuracy Possible
 - Ideal for Branching Ratio Predictions for Closely Competing Reactions
- Can be a Cost Effective Alternate to Experiments
 - Hardware & Software Efficiencies Improving Constantly
- A Balanced Approach to Kinetics Calculations Recommended





$\text{N}_2\text{H}_3 + \text{NO}_2$ Reaction Kinetics Perspective



- Radical Chemistry Modelling

- $\text{N}_2\text{H}_4/\text{NO}_2$ Auto-ignition

- Recent Works

- Only Theoretical Studies

- See Raghunath *et al.*, Adv. Quantum Chem., **69**, 253 (2014)..... $k_{298\text{ K}, 1\text{ atm}} = (2.3 \times 10^{-11})$
- See Daimon *et al.*, Sci. Tech. Energetic Materials, **74**, 17 (2013)..... $k_{298\text{ K}, 1\text{ atm}} = (1.6 \times 10^{-14})$?
- See Daimon *et al.*, J. Propul. Power, **30**, 707 (2014)..... $k_{298\text{ K}, 1\text{ atm}} = (1.9 \times 10^{-11})$

Also, See Kanno *et al.*, J. Phys. Chem., A, **119**, 7659 (2015)

$\text{CH}_3\text{NNH}_2 + \text{NO}_2 \rightarrow \text{Products}$, $k = (2.2 \times 10^{-13})$

$\text{trans-CH}_3\text{NHNH} + \text{NO}_2 \rightarrow \text{Products}$ $k = (1.4 \times 10^{-12})$

$\text{cis-CH}_3\text{NHNH} + \text{NO}_2 \rightarrow \text{Products}$ $k = (1.2 \times 10^{-12}) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

- This work (submitting for publication)

- Pulsed Laser Photolysis - Flow Tube Mass Spec Experiments

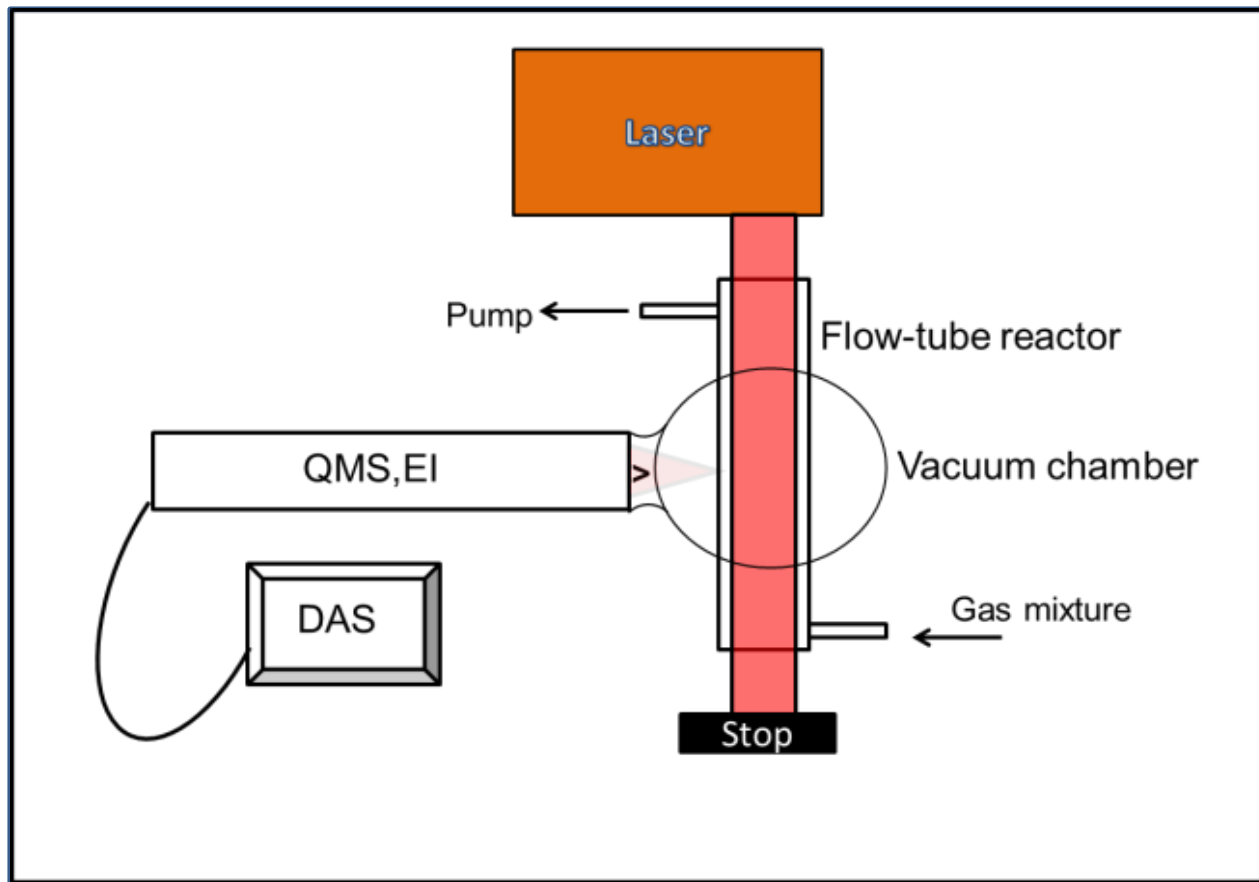
- First Experimental Determination

- Ab initio* Chemical Kinetics

- Multi-reference Second-order Perturbation and Coupled-cluster Methods: PES (Potential Energy Surface)
- Rice–Ramsperger–Kassel–Marcus Theory and Master Equation Simulations: $k(E, J)$



Pulsed Laser Photolysis Flow Tube Apparatus





N_2H_3 Source & Flow Tube Chemistry



$\text{N}_2\text{H}_4 + h\nu \rightarrow \text{N}_2\text{H}_3 + \text{H}$	$\sigma_{193\text{ nm}} = 450 \times 10^{-20} \text{ cm}^2 \text{ molec}^{-1}$	1
$\text{NO}_2 + \text{H} \rightarrow \text{NO} + \text{OH}$	$k_2 = 1.3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	2
$\text{N}_2\text{H}_4 + \text{H} \rightarrow \text{N}_2\text{H}_3 + \text{H}_2$	$k_3 = 1.4 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	3
$\text{N}_2\text{H}_4 + \text{OH} \rightarrow \text{N}_2\text{H}_3 + \text{H}_2\text{O}$	$k_4 = 3.6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	4
$\text{N}_2\text{H}_3 + \text{NO}_2 \rightarrow \text{N}_2\text{H}_2 + \text{HONO}$	k_5	5
$\text{N}_2\text{H}_3 + \text{NO}_2 \rightarrow \text{other products}$	k_6	6
$\text{HONO} \rightarrow \text{loss}$	$k_7 = 1 \text{ s}^{-1}$	7
$\text{N}_2\text{H}_3 \rightarrow \text{loss}$	$k_8 = 10 \text{ s}^{-1}$	8
$\text{H} \rightarrow \text{loss}$	$k_9 = 10 \text{ s}^{-1}$	9
$\text{OH} \rightarrow \text{loss}$	$k_{10} = 10 \text{ s}^{-1}$	10

$$[\text{HONO}] = (k_5[\text{NO}_2][\text{N}_2\text{H}_3]_0)(e^{-k_7 t} - e^{-k' t})/(k' - k_7)$$

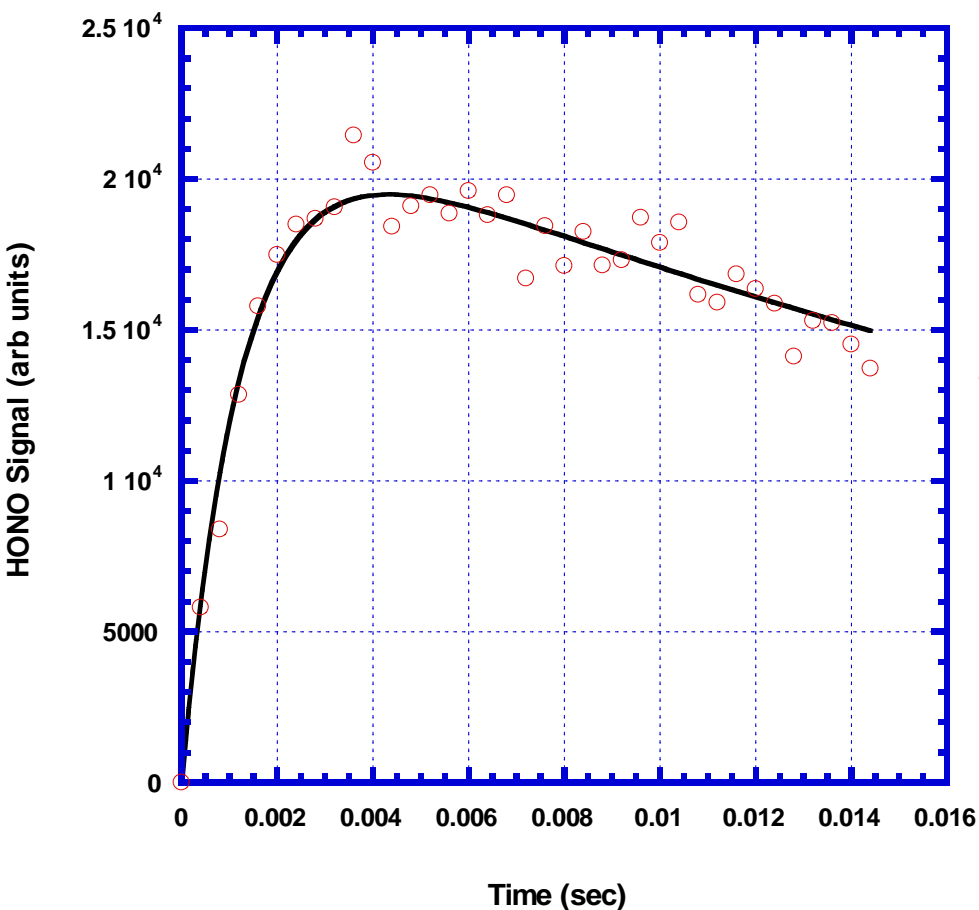
$$k' = (k_5 + k_6)[\text{NO}_2] + k_8$$

$$[\text{N}_2\text{H}_4] = 5 \times 10^{14}, [\text{H}] = 5 \times 10^{12}, [\text{NO}_2] = 1 \times 10^{13} \text{ to } 5 \times 10^{13} \text{ molecule cm}^{-3}$$

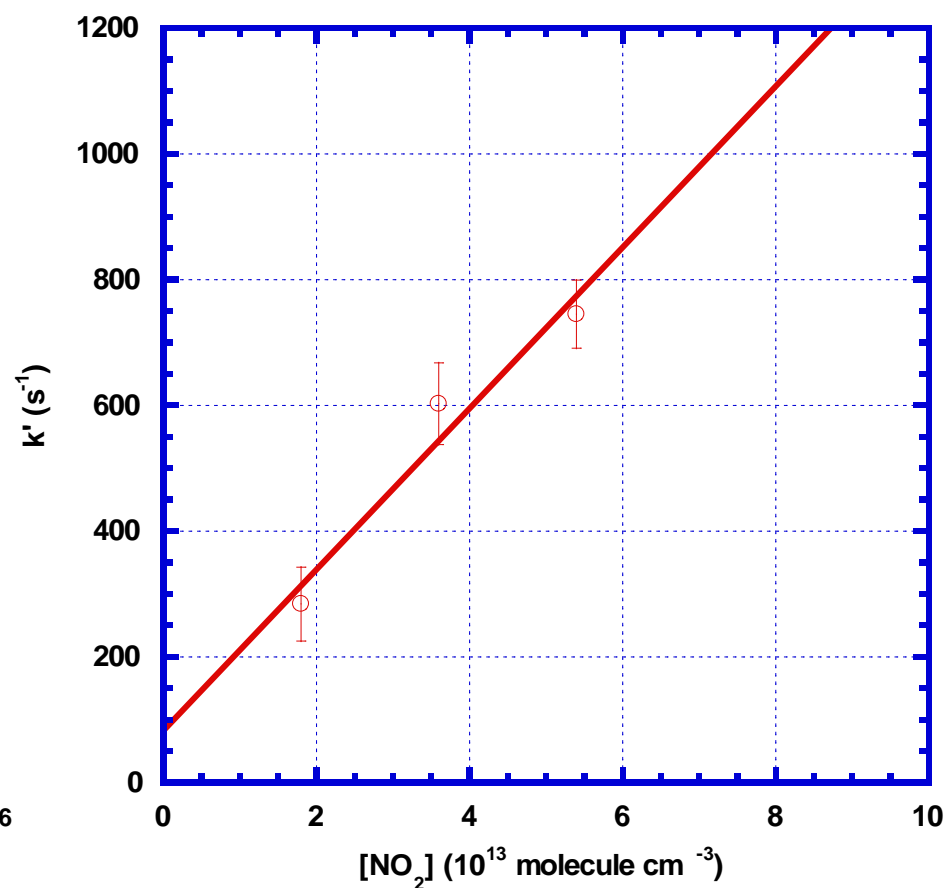


$\text{N}_2\text{H}_3 + \text{NO}_2$ Reaction Kinetics

Typical [HONO] Temporal Profile



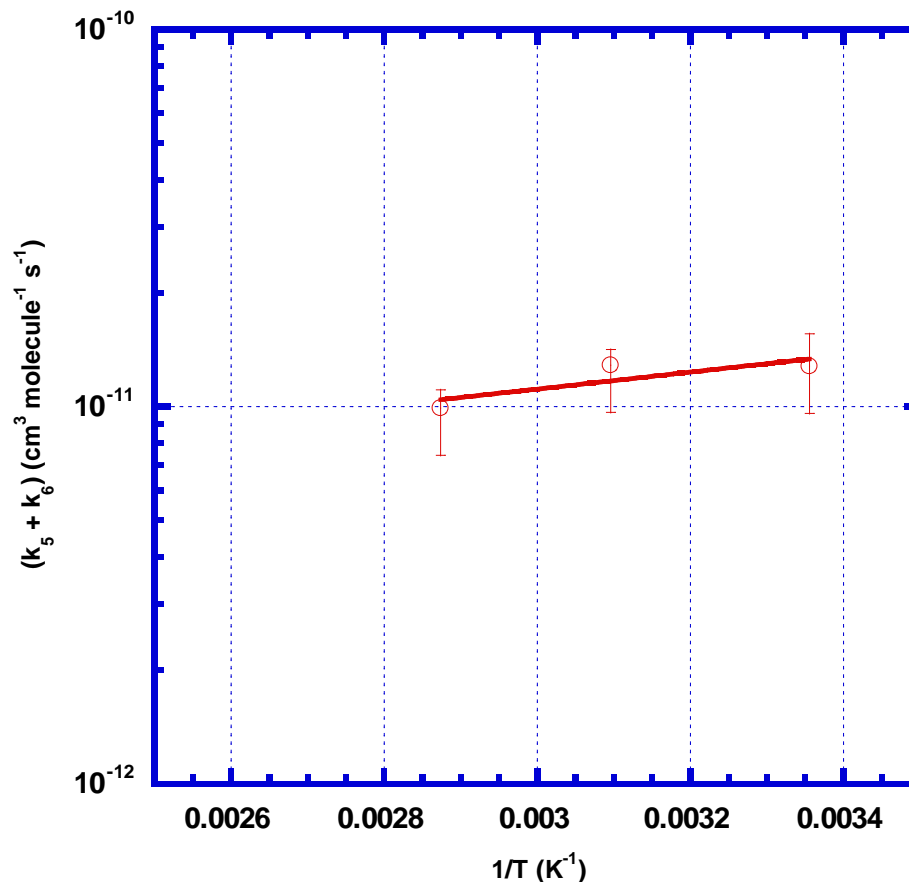
Second-order Plot



$$k_{298 \text{ K}, 2 \text{ Torr N}_2} = (1.23 \pm 0.25) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$



Temperature Dependence of $\text{N}_2\text{H}_3 + \text{NO}_2$ Reaction



$$(k_5 + k_6)_{2\text{-Torr-N}_2} = (2.36 \pm 0.47) \times 10^{-12} \exp((520 \pm 350)/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$



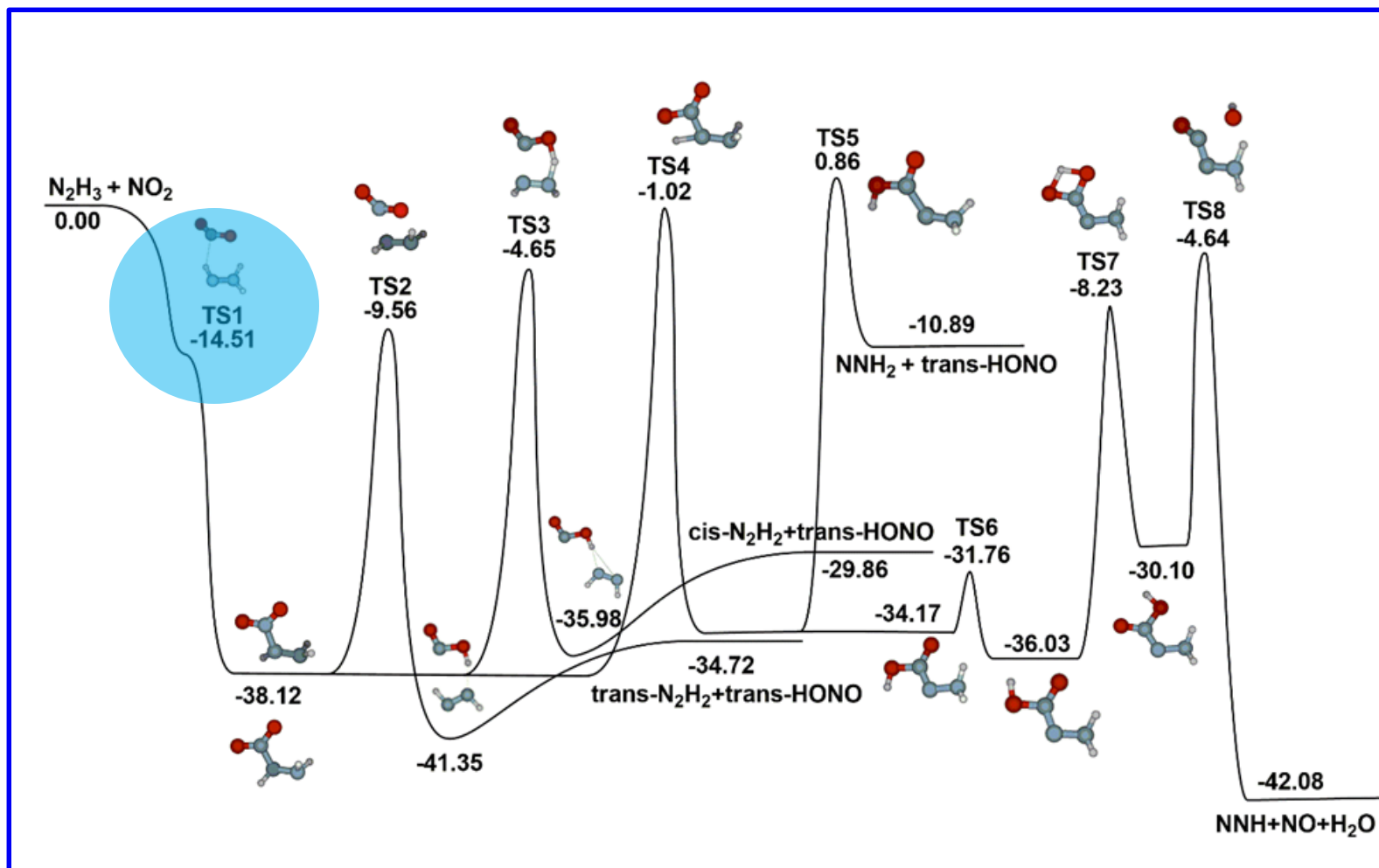
Ab initio Quantum Chemistry Approaches for $\text{N}_2\text{H}_3 + \text{NO}_2$ Reaction



- Previous Work used Single-reference Methods (e.g. CCSD(T))
- However, Reaction is not a Simple H-abstraction Process
- There is Strong Electron Repulsion Between N and O-atoms
- The Significant Multi-reference Character of the Wavefunction in the TSs for Addition and Bond Breaking With Loose Geometries Needs Proper Treatment
- Here in addition, we Apply CASPT2 With Dunning's Augmented Correlation Consistent Basis Set to Characterize the PES



Potential Energy Surface for $\text{N}_2\text{H}_3\text{NO}_2$ Adduct Formation



Zero-point corrected energies (kcal/mol, at 0 K), relative to entrance channel

CASPT2/aug-cc-pVTZ

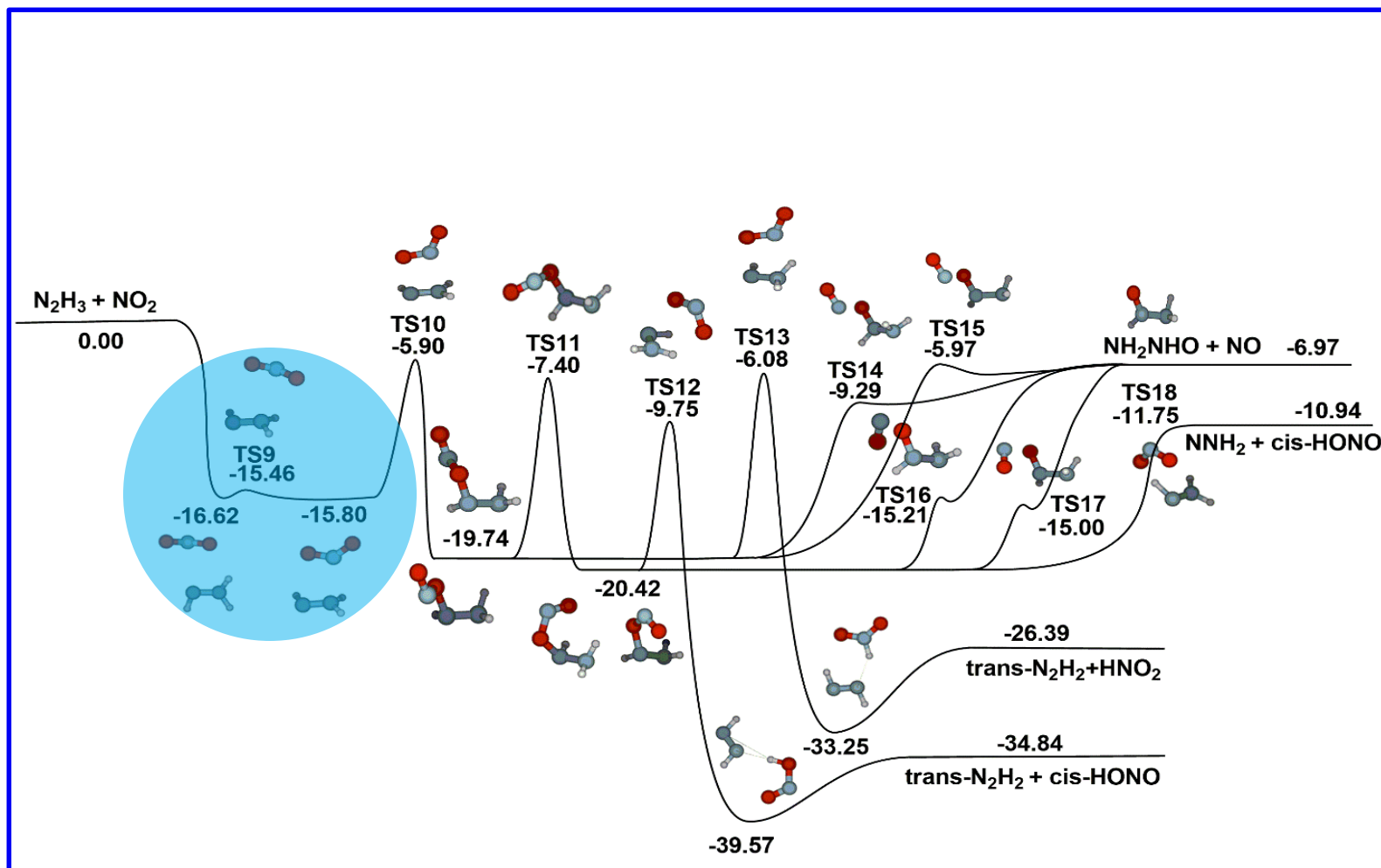
CCSD(T)/cc-pV ∞ Z

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Potential Energy Surface for $\text{N}_2\text{H}_3\text{ONO}$ Adduct Formation



Zero-point corrected energies (kcal/mol, at 0 K), relative to entrance channel

CASPT2/aug-cc-pV ∞ Z

CCSD(T)/cc-pV ∞ Z DISTRIBUTION A: Approved for public release, distribution unlimited. PA Clearance 17161

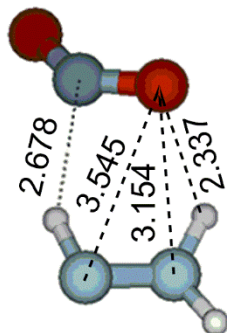




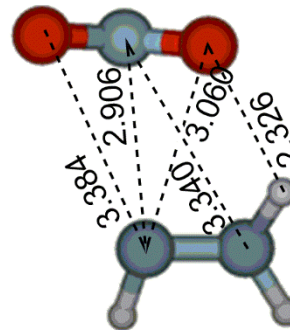
TSs and Complex Structures Involved in N_2H_3 Addition to NO_2



- Pseudo-planar 6-member ring structure
- NO_2 interaction With 2 H-atoms of N_2H_3
- TS Stabilization Two H-bonds formed

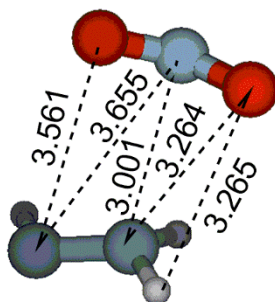


TS1

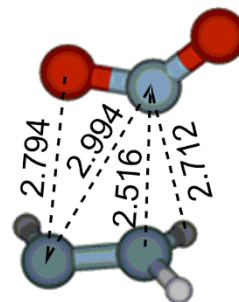


$\text{NH}_2\text{NH--NO}_2$ complex

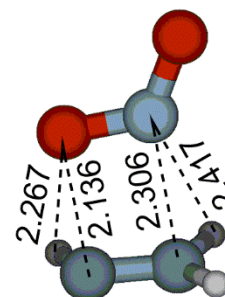
- Pseudo-planar 5-member ring structure
- One H-bond
- Loose geometry



TS9



$\text{NHH}_2\text{--NO}_2$ complex



TS10

- Planar 4-member ring structure
- Loose geometry



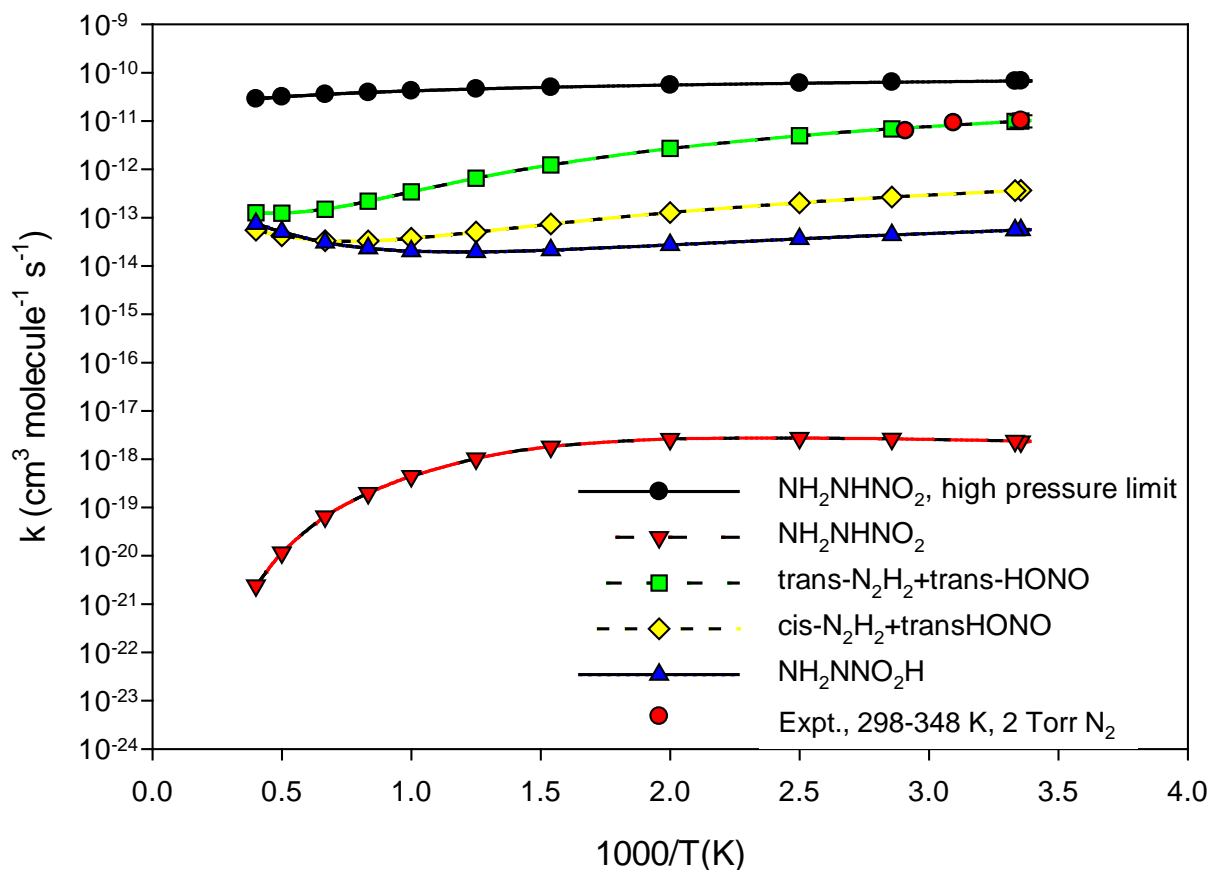
RRKM and Multi-well Simulations



- Rice–Ramsperger–Kassel–Marcus (RRKM) Theory Together With Multi-well Master Equation Simulations Carried out to Compute the Phenomenological Thermal Decomposition Rate Coefficients (Klippenstein and Co-workers, VARIFLEX, Version 2.0)
- $\Delta E_{\text{down}} = 125 \times (T/300)^{0.85} \text{ cm}^{-1}$ Energy Transfer Model Used
- TST With Rigid-rotor Harmonic-oscillator Assumption Including Tunneling Corrections Used to Calculate High-pressure Limit
- Good Agreement With Experiment Observed

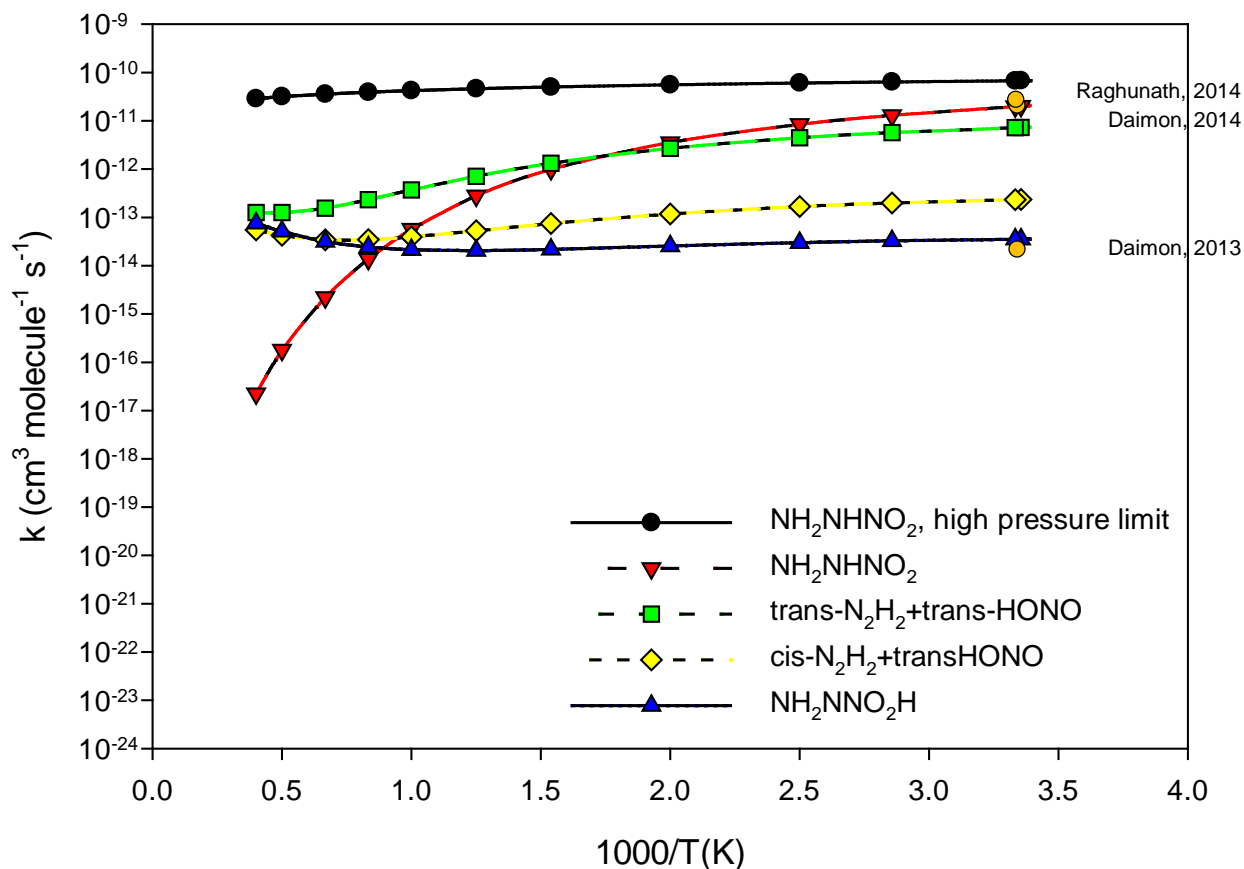


Branching Rate Coefficients (2 Torr N₂) & High Pressure Limit Versus T





Branching Rate Coefficients (1 Atm N₂) & High Pressure Limit Versus T





CH₃NH Perspective

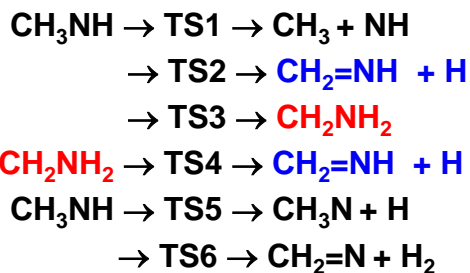


- CH₃NHNH₂ (Bipropellant Fuel)

- Pyrolysis and Oxidation Compete in Combustion Processes

- Facile Bond Breaking: CH₃NHNH₂ → CH₃NH + NH₂
 - Previously, NH₂ Monitored, Li *et al.*, Combustion Flame, 161, 16, (2014)
 - However, Fate of CH₃NH not Well Understood
 - Important for Kinetics Modelling Simulations

- CH₃NH (Decomposition, Source of H-atoms?)

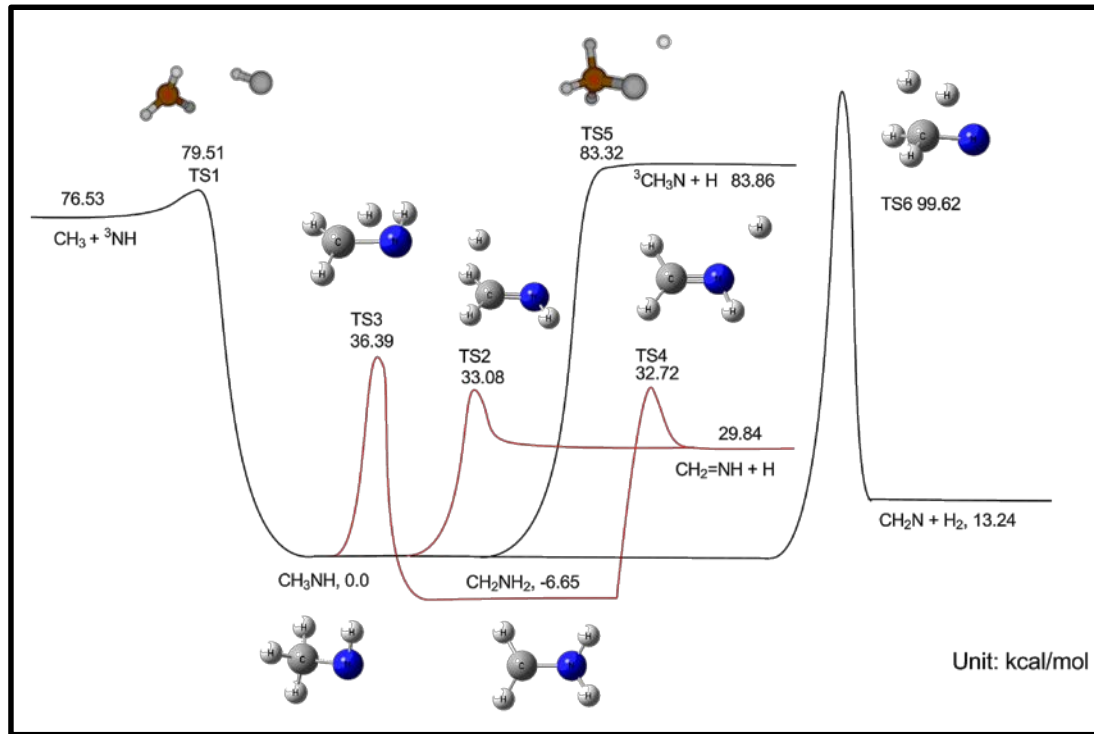


- This work

- Multi-reference *ab initio* Methods Used to Characterize Bond Breaking Processes
 - RRKM and Multi-well Simulations Carried out to Compute Reaction Rates



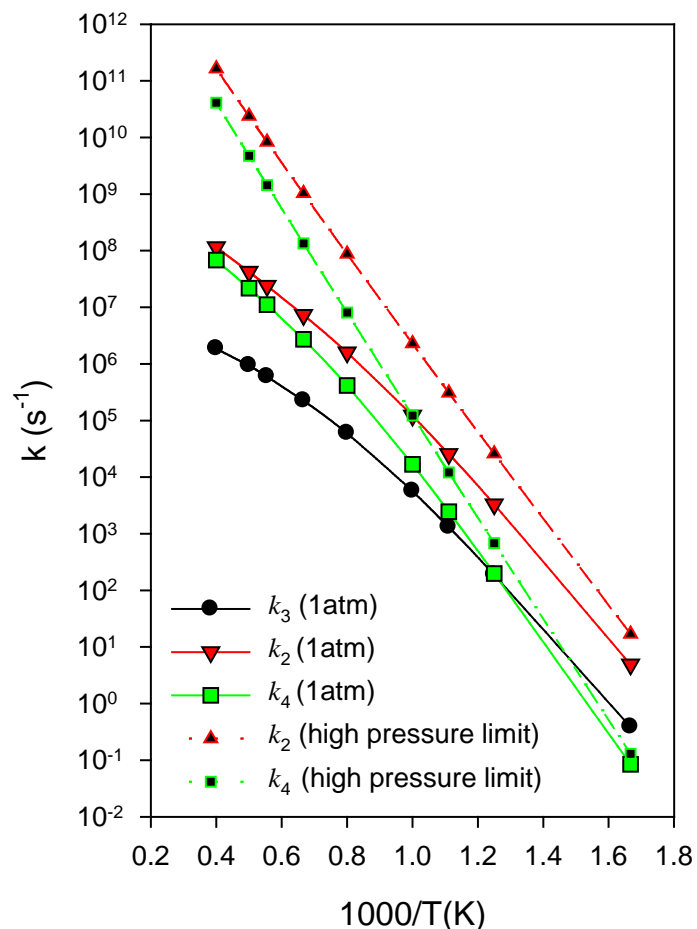
CH_3NH Dissociation PES



CASPT2 Theory for N-H and C-N Bond Breaking



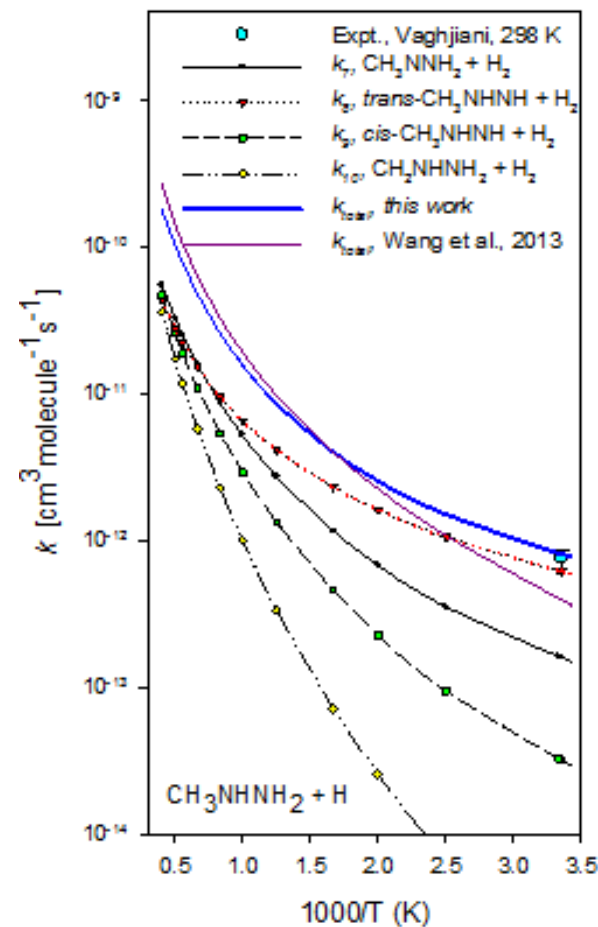
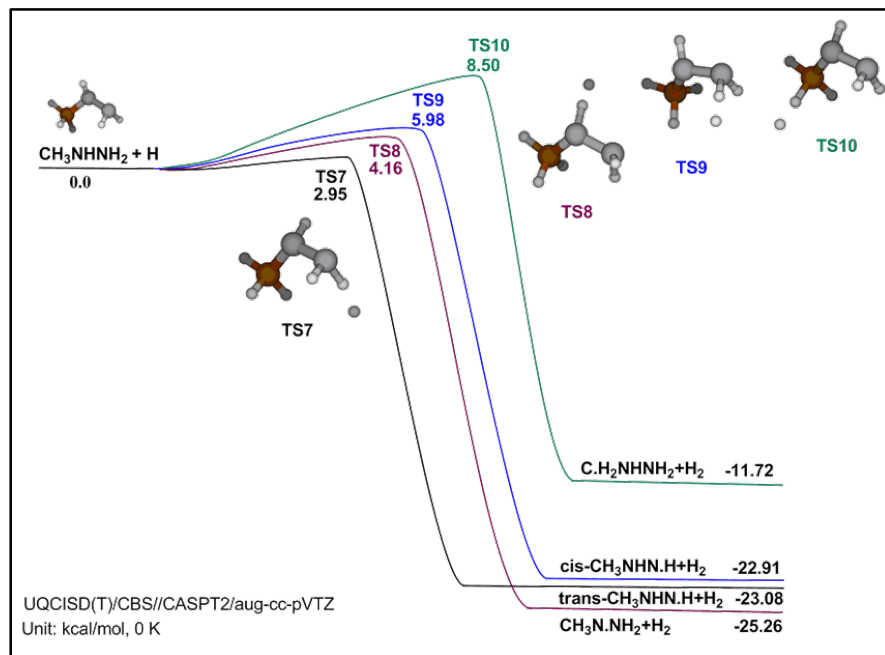
RRKM and Multi-well Simulations for CH_3NH Decomposition



Dominant Channel:
 $\text{CH}_3\text{NH} \rightarrow \text{TS2} \rightarrow \text{CH}_2=\text{NH} + \text{H}$



$\text{CH}_3\text{NHNH}_2 + \text{H}$ Reaction Kinetics Summary





Conclusions



□ $\text{N}_2\text{H}_3 + \text{NO}_2$ Reaction Kinetics

- Fast addition reaction
- Direct detection of HONO product confirmed
- Weak -ve temperature dependence of rate coefficient (k) seen
- Multi-reference methods employed to accurately determine stationary energies of the PES
- Calculated k in agreement with experiment

□ CH_3NH Decomposition

- $\text{CH}_2=\text{NH} + \text{H}$ channel dominates

□ $\text{CH}_3\text{NHNH}_2 + \text{H}$ Reaction Kinetics

- Agreement seen in absolute rate coefficient between theory and experiment
- Theory provides insight regarding at which site H-abstraction dominates

- High-level *ab initio* quantum chemical calculations and direct *real-time* kinetics measurements can provide unparalleled-details regarding the nature of the reaction mechanism of a chemical system of interest



Acknowledgements



THE NATIONAL ACADEMIES
Advisers to the Nation on Science, Engineering, and Medicine





Questions?



Solid Rocket Motors

Area 1-32

- Pad 1 & 2
- 1Mibf thrust
- 450Kibf, unique 6DOF Thrust Stand
- SOTA data acquisition system with 420 channels
- Motor sizes up to first stage ICBMs
- Extensive upgrades 2000s



Development Test History

- MM III PAP
- Sargent
- Atlas V
- Super Strypi
- MANY others



LEO-7 & LEO-46

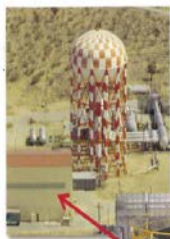
Super Strypi (SPARK) Nanosat Launcher

AFNWC Advanced 1st, 2nd & 3rd Stage



Atlas V Strap-on

Altitude/Spacecraft



Development History

- Multiple MDA systems
- Minuteman
- Agena
- MANY others

Area 1-42

Cells A, B, D

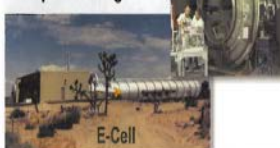
- SPEF
- Up to 50Kibf thrust
- DOF Thrust Stand
- SOTA data acquisition system with 576 channels
- 30ft diameter spacecraft altitude chamber
- Comprehensive time-resolved diagnostics (best in nation)
- Diffusion pumps
- Test large, high power Electric & Ionic Liquid Propulsion thrusters

Cell E

- Multi-Newton Chemical spacecraft thrusters to 200lbf thrust solids
- World class diagnostics system & thrust stand

In-space Laboratory

- 7 altitude chambers for in-space testing



E-Cell

For more information contact:
AFRL/RQR, 5 Pollux Dr, Edwards AFB, CA 93524
861-275-5230

MARS II Graphics

A1075 RQR testline capabilities V20

RDT&E Testing Capability

Rocket Propulsion Division

Edwards AFB, CA



Approved for Public Release, Distribution Unlimited,
PA clearance # 15416

>30 RDT&E Activities
Supported since 1990

Technology Transition Cycle

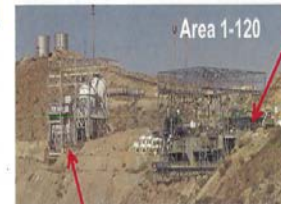


Testing Customers



Other Contractors

Liquid Rocket Engines



Area 1-120

Stand 1-A & 1-D

- 1.6Mibf Thrust stand
- Vacuum jacketed (VJ) LO2 (cryogenic) run tank, 75,000 gallon, 165 psig
- VJ LH2 (cryogenic) Run Tank, 90,000 gallon, 165 psig
- RP-1 run tank, 60,000 gal. 150 psig
- SOTA data acquisition system with 1200 channels
- Extensive upgrades 1990s



Example Run times
RS-68: 2-3 minutes

Development Test History

- Saturn V F-1
- Delta IV RS-68

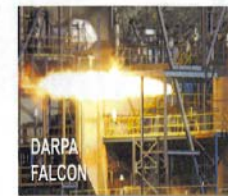
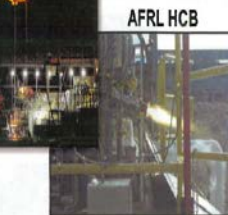


RD-68 Development

Development problems are in start-steady state-stop (transients), not long duration

Stand 2-A

- Component and engine test stand
- Two position, ground level test stand
- Maximum thrust of 2,000,000 lbf
- Horizontal or 45 degree down
- LO2 Vacuum Jacketed Run Tank; 2,000 gallon, 8,500 psig
- LH2 Vacuum Jacketed Run Tank; 3,800 gallon, 8,500 psig at 77 K
- RP-1 Run Tank, 2000 gallon, 6,600 psig
- SOTA data acquisition system with 1200 channels
- Extensive upgrades 1990-current



Development Test History

- Saturn V F-1
- DARPA FALCON
- AFRL USET turbopump
- AFRL Hydrocarbon Boost Demo (HCB)

